

Molecular basis of kinetic isotope effects

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Dynamic processes in liquid solutions—for example, molecular diffusion, ligand exchange, mineral growth, and liquid evaporation—are classic, well-studied problems in physical chemistry that are highly relevant to aqueous geochemistry and other fields (chemistry, biology, materials sciences). An important fundamental question in geochemistry is the manner in which the rate of these dynamic processes depends on solute isotopic mass, a phenomenon known as kinetic isotope fractionation [1]. The associated kinetic isotope effects are powerful investigative tools in the geosciences, but their utility could be significantly enhanced by additional understanding of their molecular basis and magnitude [2]. A complicating factor in examining these effects is that, whereas equilibrium isotope fractionation depend only on the end-points of a geochemical transformation [3], kinetic isotope fractionation depends on the mechanism and the transformation and, also, on the ratio of the gross forward rate to the net overall rate of the transformation [4].

Here, we describe efforts to use atomistic simulations (in particular, molecular dynamics simulations) to elucidate the molecular basis of kinetic isotope effects. We focus particularly on fractionation associated with diffusion, ligand exchange, electromigration, and evaporation. We show that the Newtonian mechanics of solutes in liquid water and at water-air interfaces result in significant kinetic isotope effects [5-7]. Furthermore, we show that the extent of kinetic isotope fractionation reflects the influence of collective solvation dynamics on the rates of dynamic processes in liquid solutions, an important research area in the physical chemistry of these solutions [8].

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